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(21)Application number : 2000-299996 (71)Applicant : MITSUI CHEMICALS INC
UBE IND LTD
(22)Date of filing : 29.09.2000 (72)Inventor : FUJITA TAKASHI
TAKASU ISAO

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(54) CATALYST FOR DECOMPOSITION OF ORGANIC HARMFUL SUBSTANCE AND METHOD FOR DECOMPOSING ORGANIC HALOGEN COMPOUND BY USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an inexpensive catalyst which shows higher activity and durability in the purification process of gas containing organic chlorine compounds such as dioxins, and to provide an efficient decomposition method for organic halogen compounds by using the catalyst.

SOLUTION: This catalyst for decomposition of organic compounds, particularly organic halogen compounds is prepared from water-insoluble vanadyl sulfate as the active component, and if necessary, by adding at least one oxide which contains elements selected from titanium, zirconium, niobium, molybdenum, tungsten and chromium and at least one sulfate which contains elements selected from alkaline earth metals and lead.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the catalyst which disassembles organic nature toxic substances, such as an organic halogenated compound. Furthermore, this invention relates to the catalyst which can disassemble and make harmless detrimental organic halogenated compounds generated with combustion of a municipal solid waste, industrial waste, etc., or processing of plastics, such as dioxin in exhaust gas, in detail.

[0002]

[Description of the Prior Art] In recent years, into the gas discharged from the incineration institutions which incinerate a municipal solid waste and industrial waste, or those gasification melting institutions, it became clear that organic nature toxic substances, such as an organic halogenated compound like the aromatic chlorine compound considered to be dioxin and a precursor of those, contain. Moreover, it is pointed out that organic nature toxic substances, such as bromine system dioxin, contain in exhaust gas in the case of heat-treatment of disposable-household-electric-appliances plastics. With the compound, although the toxicity differs, generally an organic halogenated compound has strong toxicity, and let it be the deadly poison on which dioxin has a remarkable bad influence, such as carrying out the disturbance of the operation of teratogenesis nature and hormone to a human body or animals and plants, especially.

[0003] Then, environmental pollution serves as a social problem and it has become pressing need to decrease the content of the organic halogenated compound of the combustion-gas middle class. Now, as the removal method of organic halogenides, such as this dioxin, the various methods of **, such as an activated-charcoal-absorption method, a thermal decomposition method, or a catalytic-cracking method by the catalyst, are proposed, for example. also in these, a catalytic-cracking method has an unnecessary secondary treatment which is needed by the adsorption process etc., when re-composition of dioxin is avoidable, since a toxic substance can be disassembled by the low temperature service 300 degrees C or less, therefore a running cost is cheap -- etc. -- it has the outstanding feature

[0004] As a catalyst used for the above-mentioned catalytic-cracking method, various metallic oxides, such as a vanadium pentoxide indicated by JP,06-38863,B or a titanium dioxide, the carbonate, and the silicate are known. However, since a high decomposition temperature and the long residence time of several minutes - several hours are needed, it is not practical. Moreover, the vanadium-pentoxide-2 titanium-oxide catalyst is indicated by JP,07-144117,A and JP,08-117557,A. However, when the catalyst containing the vanadium pentoxide was used, and SO₂ is contained in processing-object gas or it generates in a decomposition process, the oxidization activity of SO₂ becomes large. Consequently, when this is applied to purification of the exhaust gas which contains SO_x with NO_x, there is a problem that SO₃ generates so much.

[0005] moreover, such a decomposition system -- setting -- a time -- progress -- ** -- there is a problem that the fall of catalytic activity occurs. The following causes can be cited as a cause of a fall of this catalytic activity.

- 1) React with the ammonia which SO₃ generated as mentioned above added in the case of the method of returning the quality of a processing object to existence of a catalyst as reducing matter using ammonia, and a sulfur ammonium salt like an acid ammonium sulfate is accumulated on a catalyst front face, and the activity of a catalyst falls to it.
- 2) Highly, from a bird clapper, a vanadium pentoxide is returned by this, it is changed into a water-soluble vanadyl sulfate (VOSO₄ : alpha crystal type alpha-VOSO₄), and the problem said that catalytic activity falls with progress of a time also has the oxidization activity of SO₂.

3) In generating in the case where chlorine compounds (chlorine gas is included), such as HCl and Cl₂, are contained in the gas as a processing object, or a decomposition process, deterioration according [the active ingredient of a catalyst] to these chlorine compounds arises, and catalytic activity falls.

[0006] In order to solve these problems, the catalyst which made the vanadium-pentoxide-2 titanium-oxide system catalyst contain 2 tin oxide, and the catalyst which made JP,08-117557,A contain a molybdenum trioxide are proposed by JP,08-318135,A. Moreover, the catalyst which added alkali-metal sulfates, such as a barium sulfate, to vanadium-pentoxide-2 titanium oxide is indicated by JP,06-386,A, U.S. JP,5227356,B, and German JP,4419974,B. Moreover, the vanadium-pentoxide-2 titanium-oxide-3 tungstic-oxide catalyst which has resistance in the patent No. 2633316 specification to impurities, such as nitrogen oxide contained in a combustion gas, a sulfur oxide, and a heavy-metal object, is indicated. Furthermore, the catalyst which added the component of further others to vanadium-pentoxide-2 titanium oxide is indicated by JP,09-192455,A.

[0007] However, with the catalyst which contains a vanadium pentoxide as a main active ingredient, the performance about the

resistance over HCl or SO_x may not necessarily be enough, it has higher activity and higher endurance, and the catalyst for decomposition which can be offered cheaply was demanded.

[0008]

[Problem(s) to be Solved by the Invention] The purpose of this invention aims at offering cheaply the catalyst from which higher activity and higher endurance are acquired in purification processing of the gas containing organochlorine compounds, such as the above dioxin. Other purposes of this invention are to offer the efficient decomposition method of an organic halogenated compound of having used this catalyst.

[0009]

[Means for Solving the Problem] One mode of the catalyst for organic compound decomposition concerning this invention is characterized by containing an insoluble vanadyl sulfate in water. Moreover, other one modes of the catalyst for organic compound decomposition concerning this invention are characterized by including an insoluble vanadyl sulfate in at least one sort and; water containing the element chosen from the group which consists of at least one sort,; alkaline earth metal, and lead containing the element chosen from the group which consists of titanium, a zirconium, niobium, molybdenum, a tungsten, and chromium of an oxide of a sulfate.

[0010] The decomposition method of the organic halogenated compound concerning this invention is characterized by having the process which contacts an organic halogenated compound for the above-mentioned catalyst.

[0011] According to this invention, it can manufacture cheaply, and has the resistance over HCl or SO_x, and the decomposition method of the organic halogenated compound using the suitable catalyst and suitable it for purification processing of the gas containing the organic halogenated compound with which moreover more high decomposition activity is obtained can be offered.

[0012]

[Embodiments of the Invention] The catalyst concerning this invention contains an insoluble vanadyl sulfate in water at least.

[0013] An insoluble vanadyl sulfate (vanadyl sulfate : beta-VOSO₄ of beta type crystal) can be obtained in this water as a crystal which carried out green which blueness cut in itself. According to the infrared spectrum, the characteristic peak which is not seen is accepted in 940cm⁻¹ and 510cm⁻¹ by the water-soluble vanadyl sulfate (vanadyl sulfate : alpha-VOSO₄ of alpha type crystal). As for the rate of elution to the water when contacting this solid-state in water using the vanadyl sulfate of the shape of a solid-state which contains beta-VOSO₄ at least, in this invention, it is preferably desirable that it is 5% or less 10% or less.

[0014] A vanadyl sulfate insoluble in this water can be obtained by the following methods.

1) How to calcinate, after add the reducing matter, it makes a vanadium compound pentavalent in the bottom of existence of water produce sedimentation from the solution which added and obtained the ammonium salt of a sulfuric acid to this after making the valence of vanadium smaller than pentavalence, and making it dry this sedimentation. Or the method of calcinating, since sedimentation is produced from the solution which added and obtained the ammonium salt of a sulfuric acid to the vanadium compound with a valence smaller than 5 and this sedimentation is dried.

2) How to add and calcinate the ammonium salt of a sulfuric acid to oxalic acid vanadyl.

3) How to calcinate a vanadyl sulfate directly.

[0015] In addition, when using support, such as a silica, an alumina, and activated carbon, since the solution for vanadyl-sulfate formation is infiltrated into support, the vanadyl sulfate of the water-insoluble nature in the state where it was supported with calcinating by support can be obtained. Solution, vanadyl-sulfate solution, etc. which were prepared using the ammonium salt of the solution, the oxalic acid vanadyl, and the sulfuric acid which were prepared using the ammonium salt of a vanadium compound with the solution and the valence smaller than 5 which were prepared as this solution using the ammonium salt of the solution before baking obtained by the method of the above 1-3, i.e., the above-mentioned pentavalent vanadium compound, the reducing matter, and a sulfuric acid, for example, and a sulfuric acid are mentioned.

[0016] As a pentavalent vanadium compound used by the above-mentioned method of 1, at least one sort chosen from ammonium metavanadate, meta-vanadium acid, the vanadium pentoxide, etc. can be used. Moreover, as a vanadium compound with a valence smaller than 5, at least one sort of a vanadium dioxide and a vanadium trioxide can be used, for example. In these, it is most desirable from the point of the repeatability of the catalyst effect to use ammonium metavanadate as a start raw material.

[0017] As reducing matter used by the method of the above 1, even if there are few organic carboxylic acids, such as oxalic acid, a citric acid, and a tartaric acid, one sort can use suitably, for example.

[0018] The vanadyl sulfate of water-insoluble nature is that do not dissolve substantially and the feature has the decomposition activity of an organic compound in the state of tetravalence [element / V] to water including beta type crystal (beta-VOSO₄) at least. In this point, the form of an active ingredient differs from the conventional vanadium-pentoxide system catalyst according to which V element had activity in the pentavalent state fundamentally. Moreover, since it is insoluble in water, it has the resistance over HCl, and since it is a sulfate, there is resistance over SO_x.

[0019] As an ammonium salt of the sulfuric acid used for the method of the above 1 and 2, an acid ammonium sulfate, an ammonium sulfite, an ammonium sulfate, and an ammonium persulfate can be mentioned. Also in these, an ammonium sulfate is cheap, and it is desirable from the point that the target catalyst can be prepared more easily.

[0020] The vanadyl sulfate of this water-insoluble nature can be independently used for disassembly of an organic halogenated compound as a catalyst also in an organic compound.

[0021] Furthermore, a compound catalyst can be acquired to the vanadyl sulfate of this water-insoluble nature combining an

oxide and a sulfate.

[0022] This compound catalyst can be acquired by the following methods.

A) How to mix the vanadyl sulfate, oxide, and sulfate of water-insoluble nature.

B) How to calcinate after dryness, since the solution for preparing the vanadyl sulfate of water-insoluble nature into an oxide and the mixture of the solid state of a sulfate is infiltrated.

C) How to calcinate, since an oxide and a sulfate are added in the solution for preparing the vanadyl sulfate of water-insoluble nature and the obtained slurry is dried.

[0023] B) And as solution for preparing the vanadyl sulfate of the water-insoluble nature used by the method of C the solution before baking obtained by the method of 1-3 which were indicated previously -- that is The solution prepared using the ammonium salt of the above-mentioned pentavalent vanadium compound, the reducing matter, and a sulfuric acid, Solution, vanadyl-sulfate solution, etc. which were prepared using the ammonium salt of the solution, the oxalic acid vanadyl, and the sulfuric acid which were prepared using the ammonium salt of a vanadium compound with a valence smaller than 5 and a sulfuric acid are mentioned.

[0024] One or more sorts of the oxide containing the element chosen from the group which consists of titanium, a zirconium, niobium, molybdenum, a tungsten, and chromium as an oxide which is combined and is used for the vanadyl sulfate of water-insoluble nature, for example can be used. In these, 5 niobium oxides and a titanium dioxide are useful, and a titanium dioxide is the most desirable.

[0025] As the manufacture method of a titanium dioxide, conventional methods, such as a sulphate process and a chloride method, can be mentioned. Furthermore, a titanium dioxide can be obtained by calcinating intermediate fields, such as a metatitanic acid obtained in the manufacturing process in these manufacturing methods. As a form of the crystal of a titanium dioxide, although anatase type and rutile type any are sufficient, the anatase type is more desirable.

[0026] Moreover, other oxides can be manufactured using conventional methods, such as for example, a nitrate method, a sulphate process, and a chloride method. It is thought that further improvement in the resistance over HCl or SO_x and further improvement in the activity by high decentralization in the catalyst of the vanadyl sulfate as an active ingredient can be aimed at by combining such an oxide.

[0027] As a sulfate which is combined and is used for the vanadyl sulfate of the above-mentioned water-insoluble nature, one or more sorts of the sulfate chosen from the sulfate and lead sulfate of alkaline earth metal can be used, for example. As an alkaline earth metal, calcium, barium, strontium, or magnesium can be used and barium is the most desirable in these. As a barium sulfate, although the manufacture method is not limited, it can use the thing manufactured by the sedimentation method, for example or the baryta powder which ground baryte mechanically. Other sulfates could also be obtained by which manufacture method. It is thought that further improvement in the resistance over improvement in the molding intensity of a catalyst and SO_x can be aimed at by combining this sulfate.

[0028] As the blending ratio of coal between the above-mentioned 3 components, a water-insoluble nature vanadyl sulfate is 5 - 20% of the weight of a range especially preferably one to 30% of the weight preferably 0.5 to 100% of the weight, an oxide is 20 - 50% of the weight of a range preferably zero to 70% of the weight, and a sulfate can be preferably chosen from 20 - 50% of the weight of the range zero to 70% of the weight.

[0029] The temperature in the baking process for formation of the vanadyl sulfate of water-insoluble nature should just be the temperature which can form an insoluble vanadyl sulfate. By baking at low temperature, the conversion efficiency to an insoluble vanadyl sulfate falls to water, and by baking in an elevated temperature, since it is in the inclination which decomposition of an insoluble vanadyl sulfate produces in the generated water, when generating the vanadyl sulfate of more efficient water-insoluble nature, 250-500 degrees C of burning temperature are preferably chosen from the range of 300-450 degrees C.

[0030] As above-mentioned, as a catalyst concerning this invention, it is independent, the vanadyl sulfate of water-insoluble nature can be used in the state where well-known support was made to support if needed, and it can consider as a compound catalyst further at the vanadyl sulfate of water-insoluble nature combining an above-mentioned specific oxide and an above-mentioned specific sulfate, and can use in the state where well-known support was made to support if needed. The property which was further excellent in considering as such a compound catalyst in catalytic activity, endurance, moldability, etc. can be acquired.

[0031] The catalyst concerning this invention can be used for a decomposition reaction as a desired configuration. For example, it can use as configurations, such as the shape of the shape of the shape of a pellet, a globular shape, and granulatio, a tabular, and a honeycomb, and a three-dimensions mesh. A diameter can make the size in the case of-like [pellet] 1-50mm and a length of 5-60mm. Let the diameter in the case of being spherical be the range of 1-50mm. As a size in the case of-like granulatio], they are 1-40 meshes. In the case of the shape of the shape of a tabular and a honeycomb, and a three-dimensions mesh, a more desirable result can be obtained by casting in the size from which the number of cells becomes 5-400 per 1 square inch.

[0032] Such a configuration can cast the precursor of the catalyst for example, before baking, and the catalyst fine particles after baking by the conventional method, and can obtain them. When using an oxide and a sulfate as support for molding and making this support support water-insoluble nature vanadyl, the compound catalyst of a desired configuration can be acquired by what is considered as the configuration of a request of the support itself.

[0033] When the mechanical strength of a catalyst needs to be reinforced with a configuration, in the case of the shape of a tabular or a honeycomb, the additive used in molding of the catalyst of a whisker, a fiber, clay, a binder, etc. can be added according to a request. Moreover, when coating or forming a catalyst by baking on such support to the support of desired

configurations, such as the shape of a globular shape, a tabular, and a honeycomb, the catalyst of a desired configuration can be acquired by what is considered as the configuration of a request of support.

[0034] In addition, although it is desirable since, as for the total surface area of a catalyst, the one where the number of cells is larger becomes large when using it by the shape of a pellet, a globular shape, and granulatio the direction use it by the shape of the shape of a tabular and a honeycomb, and a three-dimensions mesh, when it takes into consideration the pressure loss of the gas to contact being large and becoming easy to produce plugging by the bird clapper and dust, the thing of the range of the

[0035] This can be efficiently decomposed by contacting the gas which contains the organic halogenated compound as a decomposition object in the catalyst acquired as mentioned above. As a gas containing this organic halogenated compound, the exhaust gas at the time of combustion of the time of contaminant incineration, waste, etc. can be mentioned.

[0036] As an organic halogenated compound as a decomposition object, an organic chlorine hydrocarbon compound and an organic bromine hydrocarbon compound can be mentioned, for example. As an organochlorine compound, crawl alkenes, such as crawl alkanes; crawl ethylene, such as chlorine-based dioxin; polychlorinated-biphenyls; chlorobenzene, dichlorobenzene, a chlorotoluene, a crawl phenol, and a methyl chloride, can be mentioned, for example. As an organic bromine compound, bromine alkenes, such as bromine alkanes; bromine ethylene, such as bromine system dioxin; polybrominated-biphenyls; bromine benzene, a dibromobenzene, bromine toluene, a bromine phenol, the polybromobiphenyl ether, and bromine methane, can be mentioned, for example. The catalyst of this invention can be effectively used to the gas in which these at least one sort is contained.

[0037] The temperature at the time of contact to a catalyst and a decomposition object has the desirable range of 140-300 degrees C. When reaction temperature is lower than 140 degrees C, adsorption for the catalyst of an organic halogenated compound may become strong, and decomposition efficiency may fall. Moreover, when higher than 300 degrees C, the reunion of the dioxin from a decomposition product may break out in decomposition of dioxin.

[0038] A desirable result will be obtained, if activity and decomposition processing cost are taken into consideration and space velocity will be chosen from the range of 1000-20000h-1. Furthermore, especially the range of 2000-7000h-1 is desirable.

[0039] In addition, it is better for the oxygen density in a gas to be able to perform decomposition processing in 1 - 99% of range, and to carry out by 5 - 30% of within the limits preferably.

[0040] The catalyst concerning this invention is suitable, especially when the SO_x (for example, x=1.5-3.0) itself or the component which produces SO_x during thermal decomposition processing is contained in the gas as a processing object, since it has the outstanding resistance over SO_x.

[0041] The thing of structure which has a means for discharging the gas containing the decomposition product produced in the means for introducing the gas which should be processed to the decomposition field holding a catalyst and a decomposition field as a decomposition processor using the catalyst concerning this invention, the means for contacting the introduced gas for a catalyst, and the operation of a catalyst from a decomposition field can be used. According to a request, you may perform various processings into the discharge gas after decomposition processing further.

[0042] Since the catalyst concerning this invention has the outstanding activity and outstanding endurance, prolonged continuous running of a decomposition processor is possible for it, and it can raise decomposition processing efficiency sharply.

[0043]

[Example] Hereafter, this invention is not limited by this although an example and the example of comparison explain this invention still in detail.

[0044] Ammonium metavanadate (50g) was added to examples 1-21 and the example 1 of comparison - the example (catalyst A) water of 22 catalyst manufacture, and it warmed and dissolved in 80 degrees C, and oxalic acid (125g) was added and vanadium was returned to the bottom of churning. Subsequently, the ammonium sulfate (57g) was added to the solution containing this vanadium, and the anatase type titanium dioxide (510g) and the barium sulfate (260g) were added further one by one. The obtained slurry-like solution was dried by spray dry, and powder was obtained. Little water was added and kneaded to the obtained powder, and it extruded with a length of 3mm 3mmphi and in the shape of a pellet, and cast by the extruder. After drying the obtained pellet again, it calcinated at 430 degrees C and the catalyst A included in water 9 % of the weight (beta-VOSO 4) of insoluble vanadyl sulfates, 59 % of the weight of titanium dioxides, and 32 % of the weight of barium sulfates was acquired.

((B) Catalyst) The catalyst B as well as Catalyst A was acquired except making the size of a pellet into 1.6mmphi and a length of 3mm.

((C) Catalyst) Catalyst A was pulverized and the granulatio-like catalyst C of the size of 10-20 meshes was acquired.

((D) Catalyst) Catalyst A was pulverized, the honeycomb-like catalyst whose number of cells per 1 square inch is 35 pieces was created by the conventional method using the obtained pulverization object, it started in width of face of 12mm, and length of 18cm, and Catalyst D was acquired.

((E) Catalyst) The catalyst D as well as Catalyst A was acquired except using 5 niobium oxides instead of an anatase type titanium dioxide. Catalyst D was what contains 9 % of the weight (beta-VOSO 4) of insoluble vanadyl sulfates, 59 % of the weight of 5 niobium oxides, and 32 % of the weight of barium sulfates in water.

((F) Catalyst) The catalyst F which becomes water from an insoluble vanadyl sulfate (beta-VOSO 4) as well as Catalyst A was acquired except not using an anatase type titanium dioxide and a barium sulfate.

((G) Catalyst) Ammonium metavanadate (100g) was added to water, and it warmed and dissolved in 80 degrees C, and Para tungstic-acid ammonium (103g) was added to the bottom of churning, and it dissolved. The anatase type titanium dioxide (700g)

was added to this solution, and the slurry-like solution was prepared. The obtained slurry-like solution was dried by spray dry, and powder was obtained. Little water was added and kneaded to the obtained powder, and it extruded with a length of 3mm 3mmphi and in the shape of a pellet, and cast by the extruder. After drying the obtained pellet again, it calcinated at 500 degrees C and the catalyst G included 9 % of the weight of vanadium pentoxides, 10 % of the weight of tungstic trioxides, and 81 % of the weight of titanium dioxides was acquired.

((H) Catalyst) Catalyst G was pulverized in the size of 10-20 meshes, and the granulatio-like catalyst H was acquired.

((I) Catalyst) Catalyst G was pulverized, the honeycomb-like catalyst whose number of cells per 1 square inch is 35 pieces was created by the conventional method using the pulverization object, it started in width of face of 12mm, and length of 18cm, and Catalyst I was acquired.

((J) Catalyst) Ammonium metavanadate (100g) was added to water, it warmed and dissolved in 80 degrees C, the anatase type titanium dioxide (510g) and the barium sulfate (276g) were added to this solution, and the slurry-like solution was prepared. The obtained slurry-like solution was dried by spray dry, and powder was obtained. Little water was added and kneaded to the obtained powder, and it extruded with a length of 3mm 3mmphi and in the shape of a pellet, and cast by the extruder. After drying the obtained pellet again, it calcinated at 500 degrees C and the catalyst J included in water 9 % of the weight of insoluble vanadium pentoxides, 59 % of the weight of titanium dioxides, and 32 % of the weight of barium sulfates was acquired.

((K) Catalyst) Catalyst J was pulverized in the size of 10-20 meshes, and the granulatio-like catalyst K was acquired.

((L) Catalyst) In order to check the existence of the catalysis of a titanium dioxide, the catalyst was prepared only by the titanium dioxide. The slurry-like solution which added the anatase type titanium dioxide (500g) to water, and obtained it was specifically dried by spray dry, and powder was obtained. Little water was added and kneaded to the obtained powder, and it extruded with a length of 3mm 3mmphi and in the shape of a pellet, and cast by the extruder. After drying the obtained pellet again, it calcinated at 430 degrees C and the anatase type titanium-dioxide catalyst L was acquired.

[0045] Each following examination was performed using each catalyst of the example above of an examination.

1) Decomposition activity examination 1 catalysts A, E, F, H, and J of MCB were used for it each [it], and the decomposition examination was performed to MCB. The catalyst was packed so that a capacity of 10ml might be occupied in the tubed glass reaction container of 30mmphi, the gas of composition of oxygen 10 capacity % containing MCB16ppm and nitrogen 90 capacity % was continuously passed in the reaction container, and the decomposition reaction was performed for 5 hours with space-velocity 6000hr-1 and the reaction temperature of 140-180 degrees C. The data at the time of 5-hour progress are shown in Table 1. Cracking severity (%) was analyzed using the gas chromatograph, and it asked for it by the formula of [(entrance MCB concentration-outlet MCB concentration)/(entrance MCB concentration)] x100.

[0046] Catalysts A, E, and F showed high MCB cracking severity as compared with Catalysts G, J, and L.

[0047]

[Table 1]

表1

	触媒	反応温度 (℃)	MCB分解率 (%)
実施例 1	A	180	99.9
実施例 2	A	180	99.5
実施例 3	A	140	99.0
実施例 4	E	180	98.4
実施例 5	E	160	98.1
実施例 6	E	140	97.5
実施例 7	F	180	95.8
実施例 8	F	160	95.4
実施例 9	F	140	94.0
比較例 1	G	180	86.7
比較例 2	G	160	82.5
比較例 3	G	140	78.1
比較例 4	J	180	85.2
比較例 5	J	160	80.9
比較例 6	J	140	76.5
比較例 7	L	200	0.1
比較例 8	L	180	0.0

[0048] 2) 12mm angle and the honeycomb catalyst with a length of 18cm were put in the reactor made from SUS of 13mm angle for decomposition activity examination 2 catalysts D or I of MCB, the gas of composition of oxygen 10 capacity % containing MCB16ppm and nitrogen 90 capacity % was passed continuously, and the decomposition reaction was performed with space-velocity 7000hr-1 and the reaction temperature of 200 degrees C for 5 hours. The data at the time of 5-hour progress are shown in Table 2. It asked for cracking severity (%) like the MCB decomposition activity examination 1.

[0049]

[Table 2]

表2

	触媒	反応温度 (℃)	MCB分解率 (%)
実施例 10	D	200	90.9
比較例 9	I	200	80.8

[0050] 3) The decomposition activity examination catalysts A, B, or G of DXNs were used separately, respectively, and the decomposition activity of DXNs was examined. The catalyst was packed so that a capacity of 60ml might be occupied in the reaction container made from tubed SUS of the cross section of 29mm angle, the gas of composition of oxygen 10 capacity % which contains dioxin (2378-T4CDD, 123678-H6CDD, 08CDD) so that it may become the entrance concentration of Table 3, nitrogen 80 capacity %, and steam 10 capacity % was passed continuously, and the decomposition reaction was performed for 300 hours with space-velocity 10,000hr⁻¹ and the reaction temperature of 140. The data of reaction time are shown in Table 3 for 200 to 300 hours. It asked for cracking severity (%) by the formula of [(entrance DXNs concentration-outlet DXNs concentration)/(entrance DXNs concentration)] x100.

[0051]

[Table 3]

表3

	触媒	反応温度 (°C)	入口 DXNs 濃度 (ngTEQ/Nm ³ ·h)	出口 DXNs 濃度 (ngTEQ/Nm ³ ·h)	ダイオキシン類 分解率 (%)
実施例11	A	160	12.0	0.177	98.5
実施例12	A	140	12.0	0.202	98.3
実施例13	B	140	12.0	0.032	99.7
比較例10	G	180	9.8	0.739	92.8
比較例11	G	160	9.8	0.911	90.7
比較例12	G	140	9.8	1.20	87.8

[0052] 4) In order to check the influence by the difference in the amount of HCl generated at the time of HCl-proof nature examination MCB decomposition, Put Catalysts C, H, or K in the tubed glass reaction container of 12mmphi so that it might become a capacity of 5ml, and passed continuously the gas of composition of oxygen 10 capacity % containing MCB100ppm or 16 ppm, and nitrogen 90 capacity %, it was made to decompose with space-velocity 3000hr⁻¹ and the reaction temperature of 180 degrees C, and the inclination of degradation with the passage of time was checked. Decomposition efficiency was searched for like the MCB decomposition activity examination 1. The obtained result is shown in Table 4.

[0053]

[Table 4]

表4 (MCB 分解率)

経過時間 (hr)	入口 MCB 濃度 100 ppm			入口 MCB 濃度 16 ppm		
	実施例 14	比較例 13	比較例 14	実施例 14	比較例 15	比較例 16
				触媒 C	触媒 H	触媒 K
1	99.3 (99.8)	16.0 (16.0)	34.5 (34.5)	99.7 (16.0)	86.2 (13.6)	86.5 (13.8)
25	94.3 (94.3)	49.0 (48.0)	61.1 (61.1)	99.9 (16.0)	84.2 (13.6)	85.9 (13.7)
50	92.0 (92.0)	52.9 (52.9)	63.2 (53.2)	99.8 (16.0)	83.8 (13.6)	85.2 (13.6)
76	91.1 (91.1)	52.3 (52.3)	68.5 (58.5)	99.8 (16.0)	83.6 (13.4)	84.8 (13.6)
100	91.4 (91.4)	46.8 (46.9)	62.9 (52.8)	99.4 (15.9)	88.1 (13.3)	84.6 (13.5)
125	90.8 (90.8)	50.2 (50.2)	58.7 (53.7)	—	—	—
150	91.0 (91.0)	52.8 (52.8)	68.9 (58.8)	—	—	—
175	90.6 (90.6)	50.8 (50.8)	63.5 (53.5)	—	—	—

括弧内は MCB 分解による HCl 生成量 (ppm) を示す。

[0054] 5) SO₂ oxidization activity examination catalysts A, G, or J were packed so that a capacity of 10ml might be occupied to the tubed glass reactor of 30mmphi, the gas of composition of oxygen 10 capacity % containing sulfur-dioxide 0.1 capacity %, nitrogen 79.9 capacity %, and steam 10 capacity % was passed continuously, and it was made to react for 5 hours with space-velocity 5000hr⁻¹ and the reaction temperature of 140-180 degrees C. The data at the time of a 5-hour reactivity are shown in Table 5. It asked for the oxidation quotient (%) of a sulfur dioxide by the formula of [(entrance SO₂ concentration-outlet SO₂ concentration)/(entrance SO₂ concentration)] x100.

[0055]

[Table 5]

表5

	触媒	反応温度 (°C)	SO ₂ 酸化率 (%)
実施例 16	A	180	0.4
実施例 17	A	180	0.0
実施例 18	A	140	0.0
比較例 17	G	180	2.5
比較例 18	G	160	1.8
比較例 19	G	140	1.2
比較例 20	J	180	3.3
比較例 21	J	180	2.4
比較例 22	J	140	1.8

[0056] 6) The decomposition activity examination catalysts A or G of bromine benzene are packed so that a capacity of 10ml may be occupied to the tubed glass reactor of 30mmphi, the gas of composition of oxygen 10 capacity % containing bromine benzene (MBB) 16ppm and nitrogen 90 capacity % is passed continuously, and the data at the time of 5-hour progress are shown in Table 6 with space-velocity 6000hr-1 and the reaction temperature of 140-160 degrees C. It asked for the cracking severity (%) of MBB by the formula of [(entrance MBB concentration-outlet MBB concentration)/(entrance MBB concentration)] x100.

[0057]

[Table 6]

表6

	触媒	反応温度 (℃)	MBB分解率 (%)
実施例19	A	180	98.8
実施例20	A	160	98.5
実施例21	A	140	98.1
比較例23	G	180	85.5
比較例24	G	160	80.8
比較例25	G	140	77.2

[0058]

[Effect of the Invention] According to this invention, in purification processing of the gas containing organochlorine compounds, such as the above dioxin, the catalyst from which higher activity and higher endurance are acquired can be offered cheaply. Furthermore, according to this invention, the efficient decomposition method of the organic halogenated compound using this catalyst can be offered.

[0059] Since the catalyst concerning especially this invention does not produce the oxidization to SO3 of SO2 substantially and it not only excels in activity, endurance, and SO-proof 2 sex, but it is moreover durable to HCl in disassembly of an organic halogenation compound It can use effective in efficient disassembly of the organic halogenated compound in the case where dust lives together, and the case of the gas of a processing object containing SOx and HCl, or generating these in a decomposition processing field.

[Translation done.]

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EXAMPLE

[Example] Hereafter, this invention is not limited by this although an example and the example of comparison explain this invention still in detail.

[0044] Ammonium metavanadate (50g) was added to examples 1-21 and the example 1 of comparison - the example (catalyst A) water of 22 catalyst manufacture, and it warmed and dissolved in 80 degrees C, and oxalic acid (125g) was added and vanadium was returned to the bottom of churning. Subsequently, the ammonium sulfate (57g) was added to the solution containing this vanadium, and the anatase type titanium dioxide (510g) and the barium sulfate (260g) were added further one by one. The obtained slurry-like solution was dried by spray dry, and powder was obtained. Little water was added and kneaded to the obtained powder, and it extruded with a length of 3mm 3mmphi and in the shape of a pellet, and cast by the extruder. After drying the obtained pellet again, it calcinated at 430 degrees C and the catalyst A included in water 9 % of the weight (beta-VOSO 4) of insoluble vanadyl sulfates, 59 % of the weight of titanium dioxides, and 32 % of the weight of barium sulfates was acquired.

((B) Catalyst) The catalyst B as well as Catalyst A was acquired except making the size of a pellet into 1.6mmphi and a length of 3mm.

((C) Catalyst) Catalyst A was pulverized and the granulatio-like catalyst C of the size of 10-20 meshes was acquired.

((D) Catalyst) Catalyst A was pulverized, the honeycomb-like catalyst whose number of cells per 1 square inch is 35 pieces was created by the conventional method using the obtained pulverization object, it started in width of face of 12mm, and length of 18cm, and Catalyst D was acquired.

((E) Catalyst) The catalyst D as well as Catalyst A was acquired except using 5 niobium oxides instead of an anatase type titanium dioxide. Catalyst D was what contains 9 % of the weight (beta-VOSO 4) of insoluble vanadyl sulfates, 59 % of the weight of 5 niobium oxides, and 32 % of the weight of barium sulfates in water.

((F) Catalyst) The catalyst F which becomes water from an insoluble vanadyl sulfate (beta-VOSO 4) as well as Catalyst A was acquired except not using an anatase type titanium dioxide and a barium sulfate.

((G) Catalyst) Ammonium metavanadate (100g) was added to water, and it warmed and dissolved in 80 degrees C, and Para tungstic-acid ammonium (103g) was added to the bottom of churning, and it dissolved. The anatase type titanium dioxide (700g) was added to this solution, and the slurry-like solution was prepared. The obtained slurry-like solution was dried by spray dry, and powder was obtained. Little water was added and kneaded to the obtained powder, and it extruded with a length of 3mm 3mmphi and in the shape of a pellet, and cast by the extruder. After drying the obtained pellet again, it calcinated at 500 degrees C and the catalyst G included 9 % of the weight of vanadium pentoxides, 10 % of the weight of tungstic trioxides, and 81 % of the weight of titanium dioxides was acquired.

((H) Catalyst) Catalyst G was pulverized in the size of 10-20 meshes, and the granulatio-like catalyst H was acquired.

((I) Catalyst) Catalyst G was pulverized, the honeycomb-like catalyst whose number of cells per 1 square inch is 35 pieces was created by the conventional method using the pulverization object, it started in width of face of 12mm, and length of 18cm, and Catalyst I was acquired.

((J) Catalyst) Ammonium metavanadate (100g) was added to water, it warmed and dissolved in 80 degrees C, the anatase type titanium dioxide (510g) and the barium sulfate (276g) were added to this solution, and the slurry-like solution was prepared. The obtained slurry-like solution was dried by spray dry, and powder was obtained. Little water was added and kneaded to the obtained powder, and it extruded with a length of 3mm 3mmphi and in the shape of a pellet, and cast by the extruder. After drying the obtained pellet again, it calcinated at 500 degrees C and the catalyst J included in water 9 % of the weight of insoluble vanadium pentoxides, 59 % of the weight of titanium dioxides, and 32 % of the weight of barium sulfates was acquired.

((K) Catalyst) Catalyst J was pulverized in the size of 10-20 meshes, and the granulatio-like catalyst K was acquired.

((L) Catalyst) In order to check the existence of the catalysis of a titanium dioxide, the catalyst was prepared only by the titanium dioxide. The slurry-like solution which added the anatase type titanium dioxide (500g) to water, and obtained it was specifically dried by spray dry, and powder was obtained. Little water was added and kneaded to the obtained powder, and it extruded with a length of 3mm 3mmphi and in the shape of a pellet, and cast by the extruder. After drying the obtained pellet again, it calcinated at 430 degrees C and the anatase type titanium-dioxide catalyst L was acquired.

[0045] Each following examination was performed using each catalyst of the example above of an examination.

1) Decomposition activity examination 1 catalysts A, E, F, H, and J of MCB were used for it each [it], and the decomposition examination was performed to MCB. The catalyst was packed so that a capacity of 10ml might be occupied in the tubed glass reaction container of 30mmphi, the gas of composition of oxygen 10 capacity % containing MCB16ppm and nitrogen 90

capacity % was continuously passed in the reaction container, and the decomposition reaction was performed for 5 hours with space-velocity 6000hr-1 and the reaction temperature of 140-180 degrees C. The data at the time of 5-hour progress are shown in Table 1. Cracking severity (%) was analyzed using the gas chromatograph, and it asked for it by the formula of [(entrance MCB concentration-outlet MCB concentration)/(entrance MCB concentration)] x100.

[0046] Catalysts A, E, and F showed high MCB cracking severity as compared with Catalysts G, J, and L.

[0047]

[Table 1]

表1

	触媒	反応温度 (℃)	MCB分解率 (%)
実施例1	A	180	99.9
実施例2	A	160	99.5
実施例3	A	140	99.0
実施例4	E	180	98.4
実施例5	E	160	98.1
実施例6	E	140	97.5
実施例7	F	180	95.8
実施例8	F	160	95.4
実施例9	F	140	94.0
比較例1	G	180	86.7
比較例2	G	160	82.5
比較例3	G	140	78.1
比較例4	J	180	85.2
比較例5	J	160	80.9
比較例6	J	140	76.5
比較例7	L	200	0.1
比較例8	L	180	0.0

[0048] 2) 12mm angle and the honeycomb catalyst with a length of 18cm were put in the reactor made from SUS of 13mm angle for decomposition activity examination 2 catalysts D or I of MCB, the gas of composition of oxygen 10 capacity % containing MCB16ppm and nitrogen 90 capacity % was passed continuously, and the decomposition reaction was performed with space-velocity 7000hr-1 and the reaction temperature of 200 degrees C for 5 hours. The data at the time of 5-hour progress are shown in Table 2. It asked for cracking severity (%) like the MCB decomposition activity examination 1.

[0049]

[Table 2]

表2

	触媒	反応温度 (℃)	MCB分解率 (%)
実施例10	D	200	90.9
比較例9	I	200	80.8

[0050] 3) The decomposition activity examination catalysts A, B, or G of DXNs were used separately, respectively, and the decomposition activity of DXNs was examined. The catalyst was packed so that a capacity of 60ml might be occupied in the reaction container made from tubed SUS of the cross section of 29mm angle, the gas of composition of oxygen 10 capacity % which contains dioxin (2378-T4CDD, 123678-H6CDD, 08CDD) so that it may become the entrance concentration of Table 3, nitrogen 80 capacity %, and steam 10 capacity % was passed continuously, and the decomposition reaction was performed for 300 hours with space-velocity 10,000hr-1 and the reaction temperature of 140 The data of reaction time are shown in Table 3 for 200 to 300 hours. It asked for cracking severity (%) by the formula of [(entrance DXNs concentration-outlet DXNs concentration)/(entrance DXNs concentration)] x100.

[0051]

[Table 3]

表3

	触媒	反応温度 (℃)	入口 DXNs 濃度 (ngTEQ/Nm ³ ·h)	出口 DXNs 濃度 (ngTEQ/Nm ³ ·h)	ダイオキシン類 分解率 (%)
実施例11	A	160	12.0	0.177	98.5
実施例12	A	140	12.0	0.202	98.3
実施例13	B	140	12.0	0.032	99.7
比較例10	G	180	9.8	0.739	92.8
比較例11	G	160	9.8	0.911	90.7
比較例12	G	140	9.8	1.20	87.8

[0052] 4) In order to check the influence by the difference in the amount of HCl generated at the time of HCl-proof nature examination MCB decomposition, Put Catalysts C, H, or K in the tubed glass reaction container of 12mmphi so that it might become a capacity of 5ml, and passed continuously the gas of composition of oxygen 10 capacity % containing MCB100ppm or 16 ppm, and nitrogen 90 capacity %, it was made to decompose with space-velocity 3000hr-1 and the reaction temperature of 180 degrees C, and the inclination of degradation with the passage of time was checked. Decomposition efficiency was searched for like the MCB decomposition activity examination 1. The obtained result is shown in Table 4.

[0053]

[Table 4]

表4 (MCB分解率)

経過時間 (hr)	入口MCB濃度100 ppm			入口MCB濃度10 ppm				
	実施例 14		比較例 13	比較例 14	実施例 14		比較例 15	比較例 16
	触媒 C	触媒 H	触媒 K	触媒 C	触媒 H	触媒 K		
1	99.3 (99.3)	16.0 (16.0)	34.6 (34.6)	99.7 (16.0)	86.2 (13.6)	86.5 (13.8)		
2.5	94.3 (94.3)	49.0 (49.0)	61.1 (51.1)	99.9 (16.0)	84.2 (13.5)	85.9 (13.7)		
5.0	92.0 (92.0)	52.9 (52.9)	63.2 (53.2)	99.8 (16.0)	83.8 (13.6)	85.2 (13.6)		
7.6	91.1 (91.1)	52.8 (52.8)	68.6 (58.6)	99.8 (16.0)	83.5 (13.4)	84.8 (13.6)		
10.0	91.4 (91.4)	46.8 (46.9)	52.8 (52.8)	99.4 (15.9)	83.1 (13.3)	84.6 (13.5)		
12.5	90.8 (90.8)	50.2 (50.2)	58.7 (53.7)	—	—	—		
15.0	91.0 (91.0)	52.8 (52.8)	58.9 (53.9)	—	—	—		
17.5	90.6 (90.6)	50.9 (50.9)	53.6 (53.6)	—	—	—		

括弧内はMCB分解によるHC1生成量(ppm)を示す。

[0054] 5) SO₂ oxidation activity examination catalysts A, G, or J were packed so that a capacity of 10ml might be occupied to the tubed glass reactor of 30mmphi, the gas of composition of oxygen 10 capacity % containing sulfur-dioxide 0.1 capacity %, nitrogen 79.9 capacity %, and steam 10 capacity % was passed continuously, and it was made to react for 5 hours with space-velocity 5000hr-1 and the reaction temperature of 140-180 degrees C. The data at the time of 5-hour reaction progress are shown in Table 5. It asked for the oxidation quotient (%) of a sulfur dioxide by the formula of [(entrance SO₂ concentration-outlet SO₂ concentration)/(entrance SO₂ concentration)] x100.

[0055]

[Table 5]

表5

	触媒	反応温度 (°C)	SO ₂ 酸化率 (%)
実施例 1.0	A	180	0. 4
実施例 1.7	A	160	0. 0
実施例 1.8	A	140	0. 0
比較例 1.7	G	180	2. 5
比較例 1.8	G	160	1. 6
比較例 1.9	G	140	1. 2
比較例 2.0	J	180	3. 3
比較例 2.1	J	160	2. 4
比較例 2.2	J	140	1. 8

[0056] 6) The decomposition activity examination catalysts A or G of bromine benzene are packed so that a capacity of 10ml may be occupied to the tubed glass reactor of 30mmphi, the gas of composition of oxygen 10 capacity % containing bromine benzene (MBB) 16ppm and nitrogen 90 capacity % is passed continuously, and the data at the time of 5-hour progress are shown in Table 6 with space-velocity 6000hr-1 and the reaction temperature of 140-160 degrees C. It asked for the cracking severity (%) of MBB by the formula of [(entrance MBB concentration-outlet MBB concentration)/(entrance MBB concentration)] x100.

[0057]

[Table 6]

表6

	触媒	反応温度 (°C)	MBB分解率 (%)
実施例 1.9	A	180	98. 8
実施例 2.0	A	160	98. 5
実施例 2.1	A	140	98. 1
比較例 2.3	G	180	85. 5
比較例 2.4	G	160	80. 8
比較例 2.5	G	140	77. 2

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CLAIMS

[Claim(s)]

[Claim 1] The catalyst for organic halogenated compound decomposition characterized by containing an insoluble vanadyl sulfate in water.

[Claim 2] The catalyst according to claim 1 which contains further at least one sort of the sulfate containing the element chosen from the group which consists of at least one sort, and the alkaline earth metal and lead of the oxide containing the element chosen from the group which consists of titanium, a zirconium, niobium, molybdenum, a tungsten, and chromium.

[Claim 3] The catalyst according to claim 2 which contains the aforementioned oxide zero to 70% of the weight, and contains an insoluble vanadyl sulfate in the aforementioned water for the aforementioned sulfate 0.5 to 100% of the weight zero to 70% of the weight.

[Claim 4] The catalyst according to claim 2 or 3 whose aforementioned oxide is a titanium dioxide.

[Claim 5] The catalyst according to claim 2 to 4 whose aforementioned sulfate is a barium sulfate.

[Claim 6] The catalyst according to claim 1 to 5 whose aforementioned organic halogenated compound is at least one sort of chlorine-based dioxin, polychlorinated biphenyls, crawl alkanes, crawl alkenes, bromine system dioxin, polybrominated biphenyls, bromine alkanes, and bromine alkenes.

[Claim 7] The catalyst according to claim 6 whose aforementioned organic halogenated compound is at least one sort of chlorine-based dioxin, polychlorinated biphenyls, chlorobenzene, dichlorobenzene, a chlorotoluene, a crawl phenol, a methyl chloride, the chloroethylene, bromine system dioxin, polybrominated biphenyls, bromine benzene, a dibromobenzene, bromine toluene, a bromine phenol, the polybromobiphenyl ether, bromine methane, and bromine ethylene.

[Claim 8] The decomposition method of the organic halogenated compound which is the method of disassembling the organic halogenated compound contained in a gas, and is characterized by having the process which the gas containing an organic halogenated compound is contacted for a catalyst according to claim 1 to 5, and is decomposed.

[Claim 9] The decomposition method according to claim 8 by which contact for the aforementioned organic halogenated compound and the aforementioned catalyst is performed at the temperature of 140-300 degrees C.

[Claim 10] The decomposition method according to claim 8 to 9 that the aforementioned organic halogenated compound is at least one sort of chlorine-based dioxin, polychlorinated biphenyls, crawl alkanes, crawl alkenes, bromine system dioxin, polybrominated biphenyls, bromine alkanes, and bromine alkenes.

[Claim 11] The decomposition method according to claim 10 that the aforementioned organic halogenated compound is at least one sort of chlorine-based dioxin, polychlorinated biphenyls, chlorobenzene, dichlorobenzene, a chlorotoluene, a crawl phenol, a methyl chloride, the chloroethylene, bromine system dioxin, polybrominated biphenyls, bromine benzene, a dibromobenzene, bromine toluene, a bromine phenol, the polybromobiphenyl ether, bromine methane, and bromine ethylene.

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 Active
 L1: (816) vanadyl adj sulfate
 L2: (479) oxide same (titanium or zi
 L4: (0) 3 and (haloorganic or organoh
 L5: (0) 3 and (chlorodioxin or polych
 L6: (4) 3 and (barium adj sulfate)
 L3: (111) 2 and (sulfate same (alkali
 Failed
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PAT-NO: JP02001162170A
 DOCUMENT-IDENTIFIER: JP 2001162170 A
 TITLE: CATALYST FOR DECOMPOSITION OF ORGANIC HARMFUL SUBSTANCE AND METHOD FOR DECOMPOSING ORGANIC HALOGEN COMPOUND BY USING THE SAME
 PUBN-DATE: June 19, 2001
 INVENTOR-INFORMATION:
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	U	1	Document ID	Issue Date	Pages	Title	Current OR	Current XR	Retrieval	Inventor	S	C	P	E	3	12
106	<input checked="" type="checkbox"/>		US 4002727	19770111		Desulfurization process for hydrogen sulfide-co	423/576.5	423/224; 423/226;		Sonoda, Takezo et al.	<input checked="" type="checkbox"/>					
107	<input checked="" type="checkbox"/>		US 3998765	19761221		Method of preparing phenolaldehyde foamed p	521/121	521/123; 521/128;		Novak, Viktor Alexeevich et al.	<input checked="" type="checkbox"/>					
108	<input checked="" type="checkbox"/>		US 3928179	19751223		Process for hydrorefining a residual	208/213			Gatsis, John G.	<input checked="" type="checkbox"/>					
109	<input checked="" type="checkbox"/>		US 3873580	19750325		Oxidation Process	552/221	205/552; 552/269;		Rennie, Robert Allan Campbell	<input checked="" type="checkbox"/>					
110	<input checked="" type="checkbox"/>		US 3721683	19730320		PROCESS FOR THE PREPARATION OF AROMATIC	549/239	502/170; 502/200;		Yokoyama, Ryoichi	<input checked="" type="checkbox"/>					
111	<input checked="" type="checkbox"/>	JP	20010619	9		CATALYST FOR DECOMPOSITION OF ORGANIC				FUJITA, TAKASHI et al.	<input checked="" type="checkbox"/>					
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(71)出願人 000005887
三井化学株式会社
東京都千代田区霞が関三丁目2番5号
(71)出願人 000000206
宇部興産株式会社
山口県宇部市大字小串1978番地の96
(72)発明者 藤田 壽嗣
東京都港区芝浦一丁目2番1号 シーパン
スN館 宇部興産株式会社内
(72)発明者 高須 繁
北海道旭川市神楽六条十一丁目1番13号
M S バセオ102
(74)代理人 100088328
弁理士 金田 幡之 (外2名)

(54)【発明の名称】 有機性有害物質分解触媒及びそれを用いた有機ハロゲン化合物の分解方法

(57)【要約】

【課題】 本発明の目的は、上記のようなダイオキシンなどの有機塩素化合物を含むガスの浄化処理において、より高い活性及び耐久性が得られる触媒を安価に提供することを目的とする。本発明の他の目的は、この触媒を用いた有機ハロゲン化合物の効率良い分解方法を提供すること。

【解決手段】 水に不溶性の硫酸バナジルを活性成分として、必要に応じてチタン、ジルコニウム、ニオブ、モリブデン、タンクステン及びクロムからなる群から選択された元素を含む酸化物の少なくとも1種と、アルカリ土類金属及び鉛からなる群から選択された元素を含む硫酸塩の少なくとも1種とともに有機化合物、特に有機ハロゲン化合物分解用の触媒とする。

【特許請求の範囲】

【請求項1】 水に不溶性の硫酸バナジルを含有することを特徴とする有機ハロゲン化合物分解用の触媒。

【請求項2】 チタン、ジルコニウム、ニオブ、モリブデン、タンクスチレン及びクロムからなる群から選択された元素を含む酸化物の少なくとも1種と、アルカリ土類金属及び鉛からなる群から選択された元素を含む硫酸塩の少なくとも1種と、を更に含む請求項1に記載の触媒。

【請求項3】 前記酸化物を0～70重量%、前記硫酸塩を0～70重量%、前記水に不溶性の硫酸バナジルを0.5～100重量%含む請求項2に記載の触媒。

【請求項4】 前記酸化物が二酸化チタンである請求項2または3に記載の触媒。

【請求項5】 前記硫酸塩が硫酸バリウムである請求項2～4のいずれかに記載の触媒。

【請求項6】 前記有機ハロゲン化合物が、塩素系ダイオキシン類、ポリ塩化ビフェニル類、クロルアルカン類、クロルアルケン類、臭素系ダイオキシン類、ポリ臭素化ビフェニル類、プロムアルカン類及びプロムアルケン類の少なくとも1種である請求項1～5のいずれかに記載の触媒。

【請求項7】 前記有機ハロゲン化合物が、塩素系ダイオキシン類、ポリ塩化ビフェニル類、クロルベンゼン、ジクロルベンゼン、クロルトルエン、クロルフェノール、クロルメタン、クロルエチレン、臭素系ダイオキシン類、ポリ臭素化ビフェニル類、プロムベンゼン、ジプロムベンゼン、プロムトルエン、プロムフェノール、ポリ臭化ビフェニルエーテル、プロムメタン及びプロムエチレンの少なくとも1種である請求項6に記載の触媒。

【請求項8】 気体中に含まれる有機ハロゲン化合物を分解する方法であって、有機ハロゲン化合物を含む気体を、請求項1～5のいずれかに記載の触媒に接触させて分解する工程を有することを特徴とする有機ハロゲン化合物の分解方法。

【請求項9】 前記有機ハロゲン化合物と前記触媒との接触が、140～300℃の温度で行なわれる請求項8に記載の分解方法。

【請求項10】 前記有機ハロゲン化合物が、塩素系ダイオキシン類、ポリ塩化ビフェニル類、クロルアルカン類、クロルアルケン類、臭素系ダイオキシン類、ポリ臭素化ビフェニル類、プロムアルカン類及びプロムアルケン類の少なくとも1種である請求項8～9のいずれかに記載の分解方法。

【請求項11】 前記有機ハロゲン化合物が、塩素系ダイオキシン類、ポリ塩化ビフェニル類、クロルベンゼン、ジクロルベンゼン、クロルトルエン、クロルフェノール、クロルメタン、クロルエチレン、臭素系ダイオキシン類、ポリ臭素化ビフェニル類、プロムベンゼン、ジプロムベンゼン、プロムトルエン、プロムフェノール、

ポリ臭化ビフェニルエーテル、プロムメタン及びプロムエチレンの少なくとも1種である請求項10に記載の分解方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、有機ハロゲン化合物等の有機性有害物質を分解する触媒に関する。更に詳しくは、本発明は、都市ごみや産業廃棄物などの燃焼あるいはプラスチックの処理に伴なって発生する、排ガス中のダイオキシン等の有害な有機ハロゲン化合物等を分解して無害化することのできる触媒に関する。

【0002】

【従来の技術】近年、都市ごみや産業廃棄物を焼却する焼却施設またはそれらのガス化溶融施設から排出されるガス中には、ダイオキシン類やその前駆体と考えられる芳香族塩素化合物のような有機ハロゲン化合物などの有機性有害物質が含有されていることが明らかになった。また、廃家電プラスチックの加熱処理の際に、排ガス中に臭素系ダイオキシン類などの有機性有害物質が含有されていることが指摘されている。有機ハロゲン化合物は、化合物によってその毒性は異なるものの、一般に毒性が強く、特にダイオキシン類が人体や動植物に対して毒性やホルモンの作用を攪乱するなど著しい悪影響を与える猛毒とされている。

【0003】そこで、環境汚染が社会問題となっており、燃焼排ガス中等の有機ハロゲン化合物の含有量を減少させることが急務となっている。現在、このダイオキシン等の有機ハロゲン化合物の除去方法としては、例えば活性炭吸着法、熱分解法、或は触媒による接触分解法など等の種々の方法が提案されている。これらの中でも、接触分解法は300℃以下の低温条件で有害物質を分解することができるため、ダイオキシン類の再合成を回避することができる上、吸着法などで必要とされるような二次処理が不要であり、従ってランニングコストが低廉である等、優れた特徴を有している。

【0004】上記の接触分解法に使用される触媒としては、特公平06-38863号公報に記載されている五酸化バナジウムあるいは二酸化チタン等の種々の金属酸化物、炭酸塩、ケイ酸塩が知られている。しかし、高い分解温度、数分～数時間の長い滞留時間を必要とするため実用的でない。また、特開昭07-144117号公報及び特開平08-117557号公報には五酸化バナジウム-二酸化チタン触媒が開示されている。しかしながら、五酸化バナジウムを含んだ触媒を用いると、SO₂が処理対象ガスに含まれていたり、分解工程中に発生した場合には、SO₂の酸化活性が大きくなる。その結果、NO_xとともにSO₂を含有する排ガスの浄化にこれを適用した場合には、SO₃が多量に生成するという問題がある。

【0005】また、このような分解系においては、使用

時間に経過とともに触媒活性の低下が起きるという問題がある。この触媒活性の低下の原因としては、以下の原因を挙げることができる。

1) アンモニアを還元性物質として使用して触媒の存在に処理対象物質を還元する方法の場合、上記のようにして生成したSO₃が添加したアンモニアと反応して触媒表面に酸性硫酸アンモニウムのような硫黄アンモニウム塩が蓄積して触媒の活性が低下する。

2) SO₂の酸化活性が高くなることから、これにより五酸化バナジウムが還元されて、水溶性の硫酸バナジル(α結晶型のVOSO₄ : α-VOSO₄)に変換され、使用時間の経過とともに触媒活性が低下すると言う問題もある。

3) HC1、C1₂などの塩素化合物(塩素ガスを含む)が処理対象としてのガスに含まれる場合や分解工程中に発生する場合には、触媒の活性成分がこれらの塩素化合物による変質が生じ、触媒活性が低下する。

【0006】これらの問題を解決するために、特開平08-318135号公報には五酸化バナジウム-二酸化チタン系触媒に二酸化スズを含有させた触媒や、特開平08-117557号公報に三酸化モリブデンを含有させた触媒が提案されている。また、特開平06-386号公報、米国特許5227356号公報、ドイツ特許4419974号公報には五酸化バナジウム-二酸化チタンに硫酸バリウム等のアルカリ金属硫酸塩を添加した触媒が開示されている。また、特許第2633316号明細書には、燃焼排ガス中に含まれる窒素酸化物、硫黄酸化物、重金属物などの不純物に対して耐性のある五酸化バナジウム-二酸化チタン-三酸化タンゲスタン触媒が開示されている。更に、特開平09-192455号公報には、五酸化バナジウム-二酸化チタンに更に他の成分を添加した触媒が開示されている。

【0007】しかしながら、五酸化バナジウムを主活性成分として含む触媒では、HC1やSO₂に対する耐性に関する性能が必ずしも十分でない場合があり、より高い活性及び耐久性を有し、安価に提供できる分解用の触媒が要望されていた。

【0008】

【発明が解決しようとする課題】本発明の目的は、上記のようなダイオキシンなどの有機塩素化合物を含むガスの浄化処理において、より高い活性及び耐久性が得られる触媒を安価に提供することを目的とする。本発明の他の目的は、この触媒を用いた有機ハロゲン化合物の効率良い分解方法を提供することにある。

【0009】

【課題を解決するための手段】本発明にかかる有機化合物分解用触媒の一態様は、水に不溶性の硫酸バナジルを含有することを特徴とする。また、本発明にかかる有機化合物分解用触媒の他の一態様は、チタン、ジルコニウム、ニオブ、モリブデン、タンゲスタン及びクロムから

なる群から選択された元素を含む酸化物の少なくとも1種と；アルカリ土類金属及び鉛からなる群から選択された元素を含む硫酸塩の少なくとも1種と；水に不溶性の硫酸バナジルを含むことを特徴とする。

【0010】本発明にかかる有機ハロゲン化合物の分解方法は、上記の触媒に有機ハロゲン化合物を接触させる工程を有することを特徴とする。

【0011】本発明によれば、安価に製造可能であり、かつHC1やSO₂に対する耐性を有し、しかもより高い分解活性が得られる有機ハロゲン化合物を含むガスの浄化処理に好適な触媒及びそれを用いた有機ハロゲン化合物の分解方法を提供することができる。

【0012】

【発明の実施の形態】本発明にかかる触媒は、少なくとも水に不溶性の硫酸バナジルを含むものである。

【0013】この水に不溶性の硫酸バナジル(β型結晶の硫酸バナジル: β-VOSO₄)とは、それ自体青味がかった緑色をした結晶として得ることができるものである。赤外線スペクトルによると、940 cm⁻¹及び510 cm⁻¹に水溶性硫酸バナジル(α型結晶の硫酸バナジル: α-VOSO₄)には見られない特徴的なピークが認められる。本発明においては、少なくともβ-VOSO₄を含む固体状の硫酸バナジルを用いるものであり、この固体を水と接触させたときの水への溶出率は10%以下、好ましくは5%以下であることが望ましい。

【0014】この水に不溶性の硫酸バナジルは、例えば以下の方法によって得ることができる。

1) 水の存在下で5価のバナジウム化合物に、還元性物質を加え、バナジウムの原子価を5価より小さくしてからこれに硫酸のアンモニウム塩を添加して得た水溶液から沈澱を生じさせ、この沈澱を乾燥させてから焼成する方法。あるいは、原子価が5よりも小さいバナジウム化合物に硫酸のアンモニウム塩を添加して得た水溶液から沈澱を生じさせ、この沈澱を乾燥させてから焼成する方法。

2) シュウ酸バナジルに硫酸のアンモニウム塩を添加して焼成する方法。

3) 硫酸バナジルを直接焼成する方法。

【0015】なお、シリカ、アルミナ、活性炭等の担体を用いる場合は、担体に、硫酸バナジル形成用の水溶液を含浸させてから、焼成することで、担体に担持された状態の水不溶性の硫酸バナジルを得ることができる。この水溶液としては、例えば、上記1)～3)の方法で得られる焼成前の水溶液、すなわち、上記の5価のバナジウム化合物、還元性物質及び硫酸のアンモニウム塩を用いて調製した水溶液、原子価が5よりも小さいバナジウム化合物及び硫酸のアンモニウム塩を用いて調製した水溶液、シュウ酸バナジル及び硫酸のアンモニウム塩を用いて調製した水溶液及び硫酸バナジル水溶液等が挙げられる。

【0016】上記の1)の方法で用いられる5価のバナジウム化合物としては、メタバナジン酸アンモニウム、メタバナジン酸、五酸化バナジウム等から選択した少なくとも1種を用いることができる。また、原子価が5よりも小さいバナジウム化合物としては、例えば、二酸化バナジウム及び三酸化バナジウムの少なくとも1種を用いることができる。これらの中では、メタバナジン酸アンモニウムを出発原料とすることが、触媒効果の再現性の点から最も好ましい。

【0017】上記1)の方法で用いられる還元性物質としては、例えば、シュウ酸、クエン酸及び酒石酸などの有機カルボン酸の少なくとも1種が好適に利用できる。

【0018】水不溶性の硫酸バナジルは少なくとも β 型結晶(β -VOSO₄)を含むもので、その特徴は、水に対して実質的に溶解せず、かつV元素が4価の状態で有機化合物の分解活性を有していることである。この点において、V元素が5価の状態で活性を有していた従来の五酸化バナジウム系触媒とは根本的に活性成分の形態が異なっている。また、水に不溶性であるため、HC1に対する耐性を有し、また、硫酸塩であるためにSO₄²⁻に対する耐性もある。

【0019】上記1)及び2)の方法に用いられる硫酸のアンモニウム塩としては、酸性硫酸アンモニウム、亜硫酸アンモニウム、硫酸アンモニウム及び過硫酸アンモニウムを挙げることができる。これらの中でも、硫酸アンモニウムが安価であり、また、目的とした触媒をより容易に調製できるという点から好ましい。

【0020】この水不溶性の硫酸バナジルを単独で触媒として、有機化合物、中でも有機ハロゲン化合物の分解に用いることができる。

【0021】更に、この水不溶性の硫酸バナジルに、酸化物及び硫酸塩を組合せて複合触媒を得ることができる。

【0022】この複合触媒は、以下のような方法によって得ることができる。

A) 水不溶性の硫酸バナジル、酸化物及び硫酸塩を混合する方法。

B) 酸化物と硫酸塩の固体状態の混合物に、水不溶性の硫酸バナジルを調製するための水溶液を含浸させてから、乾燥後、焼成する方法。

C) 水不溶性の硫酸バナジルを調製するための水溶液中に酸化物及び硫酸塩を添加し、得られたスラリーを乾燥させてから、焼成する方法。

【0023】B)及びC)の方法で用いられる水不溶性の硫酸バナジルを調製するための水溶液としては、先に記載した1)～3)の方法で得られる焼成前の水溶液、すなわち、上記の5価のバナジウム化合物、還元性物質及び硫酸のアンモニウム塩を用いて調製した水溶液、原子価が5よりも小さいバナジウム化合物及び硫酸のアンモニウム塩を用いて調製した水溶液、シュウ酸バナジル及

び硫酸のアンモニウム塩を用いて調製した水溶液及び硫酸バナジル水溶液等が挙げられる。

【0024】水不溶性の硫酸バナジルに組み合せて用いる酸化物としては、例えば、チタン、ジルコニウム、ニオブ、モリブデン、タンクスチタン及びクロムからなる群から選択した元素を含む酸化物の1種以上を用いることができる。これらの中では、五酸化ニオブ及び二酸化チタンが有用であり、二酸化チタンが最も好ましい。

【0025】二酸化チタンの製造方法としては、硫酸塩法や塩化物法などの常法を挙げることができる。更に、これらの製造法における製造工程中で得られるメタチタン酸等の中間体を焼成することによって二酸化チタンを得ることができる。二酸化チタンの結晶の形態としては、アナターゼ型、ルチル型のいずれでも良いが、アナターゼ型の方が好ましい。

【0026】また、他の酸化物は、例えば硝酸塩法、硫酸塩法、塩化物法などの常法を用いて製造することができる。このような酸化物を組合せることで、HC1やSO₄²⁻に対する耐性の更なる向上や、活性成分としての硫酸バナジルの触媒中の高分散化による活性の更なる向上を図ると考えられる。

【0027】上記の水不溶性の硫酸バナジルに組み合せて用いる硫酸塩としては、例えば、アルカリ土類金属の硫酸塩及び硫酸鉛から選択した硫酸塩の1種以上を用いることができる。アルカリ土類金属としては、カルシウム、バリウム、ストロンチウムあるいはマグネシウムを用いることができ、これらの中ではバリウムが最も好ましい。硫酸バリウムとしては、その製造方法は限定されないが、例えば沈降法により製造されたもの、または重

30 晶石を機械的に粉砕したバライド粉等を使用することができる。その他の硫酸塩もいずれの製造方法で得られたものでもよい。この硫酸塩を組み合せることで、触媒の成型強度の向上、SO₄²⁻に対する耐性の更なる向上が図れるものと考えられる。

【0028】上記の3成分間の配合割合としては、水不溶性硫酸バナジルは0.5～100重量%、好ましくは1～30重量%、特に好ましくは5～20重量%の範囲で、酸化物は0～70重量%、好ましくは20～50重量%の範囲で、硫酸塩は0～70重量%、好ましくは2

40 0～50重量%の範囲から選択することができる。

【0029】水不溶性の硫酸バナジルの形成のための焼成工程における温度は、不溶性の硫酸バナジルが形成可能な温度であればよい。低温での焼成では、水に不溶性の硫酸バナジルへの変換効率が低下し、高温での焼成では生成した水に不溶性の硫酸バナジルの分解が生じる傾向にがあるので、より効率的な水不溶性の硫酸バナジルの生成を行なう上では、250～500°C、好ましくは300～450°Cの範囲から焼成温度を選択する。

【0030】上述のとおり、本発明にかかる触媒としては水不溶性の硫酸バナジルを単独で、必要に応じて公知

の担体に担持させた状態で用いることができ、更に、水不溶性の硫酸バナジルに上記の特定の酸化物及び硫酸塩を組合せて複合触媒とし、必要に応じて公知の担体に担持させた状態で用いることができる。このような複合触媒とすることで、更に触媒活性や耐久性、成型性などにおいて優れた特性を得ることができる。

【0031】本発明にかかる触媒は所望の形状として分解反応に用いることができる。例えば、ペレット状、球状、顆粒状、板状、ハニカム状、三次元網目状などの形状として利用することができる。ペレット状の場合における大きさは、例えば、直径が1~50mm、長さ5~60mmとすることができる。球状の場合の直径は、例えば1~50mmの範囲とすることができる。顆粒状の場合の大きさとしては、1~40メッシュとすることができます。板状、ハニカム状、三次元網目状の場合は、そのセル数が1平方インチ当たり5~400個となる大きさに成型することにより好ましい結果を得ることができる。

【0032】このような形状は、例えば焼成前の触媒の前駆体や焼成後の触媒粉体を常法により成型して得ることができます。酸化物及び硫酸塩を成型用の担体として利用し、この担体に水不溶性バナジルを担持させる場合には、担体自体を所望の形状としておくことで、所望の形状の複合触媒を得ることができます。

【0033】形状によって触媒の機械的強度を補強する必要がある場合は、例えば板状やハニカム状の場合には、ウイスカー、ファイバー、粘土、バインダー等の触媒の成型において利用されている添加物を所望に応じて添加することができる。また、球状、板状、ハニカム状などの所望の形状の担体に対して触媒をコーティングする、あるいはこのような担体上で焼成により形成する場合は、担体を所望の形状としておくことで、所望の形状の触媒を得ることができます。

【0034】なお、ペレット状、球状、顆粒状で使用する場合は粒径は小さい方が、また、板状、ハニカム状、三次元網目状で使用する場合はセル数が大きい方が、触媒の総表面積は大きくなるので好ましいが、接触させるガスの圧力損失が大きくなることやダストによる詰まりが生じ易くなる場合があることを考慮すると、上述した大きさの範囲のものが好ましい。

【0035】以上のようにして得られた触媒に、分解対象物としての有機ハロゲン化合物を含む気体を接触させることでこれを効率良く分解することができる。この有機ハロゲン化合物を含む気体としては、ごみ焼却時や廃棄物等の燃焼時の排ガスを挙げることができる。

【0036】分解対象物としての有機ハロゲン化合物としては、例えば、有機塩素炭化水素化合物及び有機臭素炭化水素化合物を挙げることができる。有機塩素化合物としては、例えば塩素系ダイオキシン類；ポリ塩化ビフェニル類；クロルベンゼン、ジクロルベンゼン、クロル

トルエン、クロルフェノール、クロルメタン等のクロルアルカン類；クロルエチレン等のクロルアルケン類等を挙げることができる。有機臭素化合物としては、例えば、臭素系ダイオキシン類；ポリ臭素化ビフェニル類；プロムベンゼン、ジプロムベンゼン、プロムトルエン、プロムフェノール、ポリ臭化ビフェニルエーテル、プロムメタン等のプロムアルカン類；プロムエチレン等のプロムアルケン類などを挙げができる。これらの少なくとも1種が含まれる気体に対して本発明の触媒は有效地に利用できる。

【0037】触媒と分解対象物との接触時の温度は、140~300°Cの範囲が好ましい。反応温度が140°Cより低い場合、有機ハロゲン化合物の触媒への吸着が強くなり分解効率が低下する場合がある。また、300°Cよりも高い場合、ダイオキシン類の分解では分解物からのダイオキシン類の再結合が起きる場合がある。

【0038】空間速度は、活性及び分解処理コストを考慮すれば、1000~20000h⁻¹の範囲から選択すると好ましい結果が得られる。さらには、2000~7000h⁻¹の範囲が特に好ましい。

【0039】なお、気体中の酸素濃度は、1~99%の範囲で分解処理を行なうことができ、好ましくは5~30%の範囲内で行なう方がよい。

【0040】本発明にかかる触媒は、SO_xに対する優れた耐性を有しているので、処理対象としての気体中にSO_x（例えばx=1.5~3.0）自体、あるいは加熱分解処理中にSO_xを生じる成分が含まれている場合に特に好適である。

【0041】本発明にかかる触媒を用いた分解処理装置としては、触媒を保持する分解領域と、分解領域に処理すべき気体を導入するための手段と、導入された気体を触媒と接触させるための手段と、触媒の作用で生じた分解物を含む気体を分解領域から排出するための手段を有する構造のものが利用できる。分解処理後の排出気体には、更に所望に応じて各種処理を行なってよい。

【0042】本発明にかかる触媒は優れた活性及び耐久性を有するので、分解処理装置の長時間連続運転が可能であり、分解処理効率を大幅に向上させることができると。

40 【0043】

【実施例】以下、実施例、比較例によって本発明を更に詳細に説明するが、本発明はこれによって限定されるものではない。

【0044】実施例1~21及び比較例1~22

触媒製造例

（触媒A）水にメタバナジン酸アンモニウム（50g）を加え、80°Cに加温して溶解し、攪拌下にシュウ酸（125g）を加えてバナジウムを還元した。次いで、このバナジウムを含む溶液に硫酸アンモニウム（57g）を加え、更にアナターゼ型二酸化チタン（510

g) 及び硫酸バリウム (260 g) を順次加えた。得られたスラリー状溶液をスプレードライで乾燥させて粉末を得た。得られた粉末に少量の水を加えて混練し、押出し機で3mmΦ、長さ3mmのペレット状に押し出して成型した。得られたペレットを再度乾燥させた後、430°Cで焼成し、水に不溶性の硫酸バナジル (β -VOSO₄) 9重量%、二酸化チタン59重量%、硫酸バリウム32重量%含む触媒Aを得た。

(触媒B) ペレットの大きさを1.6mmΦ、長さ3mmとする以外は触媒Aと同様にして触媒Bを得た。

(触媒C) 触媒Aを粉碎し、10~20メッシュの大きさの顆粒状触媒Cを得た。

(触媒D) 触媒Aを粉碎し、得られた粉碎物を用いて1平方インチ当りのセル数が35個のハニカム状触媒を常法により作成し、幅12mm、長さ18cmに切り出して触媒Dを得た。

(触媒E) アナターゼ型二酸化チタンの代わりに五酸化ニオブを用いる以外は触媒Aと同様にして触媒Dを得た。触媒Dは、水に不溶性の硫酸バナジル (β -VOSO₄) 9重量%、五酸化ニオブ59重量%、硫酸バリウム32重量%を含むものであった。

(触媒F) アナターゼ型二酸化チタン及び硫酸バリウムを用いない以外は触媒Aと同様にして、水に不溶性の硫酸バナジル (β -VOSO₄) からなる触媒Fを得た。

(触媒G) 水にメタバナジン酸アンモニウム (100 g) を加え、80°Cに加温して溶解し、攪拌下にバラタングステン酸アンモニウム (103 g) を加えて溶解した。この溶液にアナターゼ型二酸化チタン (700 g) を加えてスラリー状溶液を調製した。得られたスラリー状溶液をスプレードライで乾燥させて粉末を得た。得られた粉末に少量の水を加えて混練し、押出し機で3mmΦ、長さ3mmのペレット状に押し出して成型した。得られたペレットを再度乾燥させた後、500°Cで焼成し、五酸化バナジウム9重量%、三酸化タングステン10重量%、二酸化チタン81重量%含む触媒Gを得た。

(触媒H) 触媒Gを10~20メッシュの大きさに粉碎し、顆粒状触媒Hを得た。

(触媒I) 触媒Gを粉碎し、粉碎物を用いて1平方インチ当りのセル数が35個のハニカム状触媒を常法により作成し、幅12mm、長さ18cmに切り出して触媒I

を得た。

(触媒J) 水にメタバナジン酸アンモニウム (100 g) を加え、80°Cに加温して溶解し、この溶液にアナターゼ型二酸化チタン (510 g) 及び硫酸バリウム (276 g) を加えてスラリー状溶液を調製した。得られたスラリー状溶液をスプレードライで乾燥させて粉末を得た。得られた粉末に少量の水を加えて混練し、押出し機で3mmΦ、長さ3mmのペレット状に押し出して成型した。得られたペレットを再度乾燥させた後、50

10°Cで焼成し、水に不溶性の五酸化バナジウム9重量%、二酸化チタン59重量%、硫酸バリウム32重量%含む触媒Jを得た。

(触媒K) 触媒Jを10~20メッシュの大きさに粉碎し、顆粒状触媒Kを得た。

(触媒L) 二酸化チタンの触媒作用の有無を確認するため、二酸化チタンのみで触媒を調製した。具体的には、アナターゼ型二酸化チタン (500 g) を水に加えて得たスラリー状溶液をスプレードライで乾燥させて粉末を得た。得られた粉末に少量の水を加えて混練し、押出し機で3mmΦ、長さ3mmのペレット状に押し出して成型した。得られたペレットを再度乾燥させた後、430°Cで焼成し、アナターゼ型二酸化チタン触媒Lを得た。

【0045】試験例

上記の各触媒を用いて、以下の各試験を行なった。

1) MCBの分解活性試験1

触媒A、E、F、H及びJをそれぞれ個々に用いてMCBに分解試験を行なった。触媒を30mmΦの筒状ガラス製反応容器に10mlの容積を占めるように詰め、MCB 16 ppmを含む酸素10容積%、窒素90容積%の組成のガスを反応容器中に連続的に流し、空間速度6000hr⁻¹、反応温度140~180°Cで5時間分解反応を行なった。5時間経過時のデータを表1に示す。分解率(%)は、ガスクロマトグラフを用いて分析し、[(入口MCB濃度-出口MCB濃度)/(入口MCB濃度)] × 100の計算式により求めた。

【0046】触媒A、E、Fは触媒G、J、Lと比較して高いMCB分解率を示した。

【0047】

【表1】

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表1

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	触媒	反応温度(℃)	MCB分解率(%)
実施例1	A	180	99.9
実施例2	A	160	99.5
実施例3	A	140	99.0
実施例4	E	180	98.4
実施例5	E	160	98.1
実施例6	E	140	97.5
実施例7	F	180	95.8
実施例8	F	160	95.4
実施例9	F	140	94.0
比較例1	G	180	86.7
比較例2	G	160	82.5
比較例3	G	140	78.1
比較例4	J	180	85.2
比較例5	J	160	80.9
比較例6	J	140	76.5
比較例7	L	200	0.1
比較例8	L	180	0.0

【0048】2) MCBの分解活性試験2

触媒DまたはIを13mm角のSUS製反応器に1.2m
m角、長さ18cmのハニカム触媒を詰め、MCB 16
ppmを含む酸素10容量%、窒素90容量%の組成の
ガスを連続的に流し、空間速度7000hr⁻¹、反応温*

*度200℃で5時間分解反応を行なった。5時間経過時のデータを表2に示す。分解率(%)はMCB分解活性試験1と同様にして求めた。

【0049】

【表2】

	触媒	反応温度(℃)	MCB分解率(%)
実施例10	D	200	90.9
比較例9	I	200	80.8

【0050】3) DXNsの分解活性試験

触媒A、BまたはGをそれぞれ個々に用い、DXNsの分解活性を試験した。触媒を29mm角の断面の筒状SUS製反応器に60mlの容積を占めるように詰め、ダイオキシン類(2378-T4CDD、123678-H6CDD、08CDD)を表3の入口濃度となるよう含む、酸素10容量%、窒素80容量%、水蒸気10容量%の組成のガスを連続的に流し、空間速度10、*

※000hr⁻¹、反応温度140～180℃で300時間分解反応を行なった。200～300時間反応時のデータを表3に示す。分解率(%)は、[(入口DXNs濃度-出口DXNs濃度)/(入口DXNs濃度)]×100の計算式により求めた。

【0051】

【表3】

	触媒	反応温度(℃)	入口DXNs濃度(ngTEQ/Nm ³ ·h)	出口DXNs濃度(ngTEQ/Nm ³ ·h)	ダイオキシン類分解率(%)
実施例11	A	160	12.0	0.177	98.5
実施例12	A	140	12.0	0.202	98.3
実施例13	B	140	12.0	0.032	99.7
比較例10	G	180	9.8	0.739	92.8
比較例11	G	160	9.8	0.911	90.7
比較例12	G	140	9.8	1.20	87.8

【0052】4) 耐HC1性試験

MCB分解時に生成するHC1の量の違いによる影響を確認するために、触媒C、HまたはKを12mmΦの筒状ガラス製反応器に5mlの容積になるように詰め、MCB 100ppmまたは16ppmを含む、酸素10容量%、窒素90容量%の組成のガスを連続的に流し、★

★空間速度3000hr⁻¹、反応温度180℃で分解させ、経時劣化の傾向を確認した。分解効率はMCB分解活性試験1と同様にして求めた。得られた結果を表4に示す。

【0053】

【表4】

表4 (MCB分解率)

経過時間 (hr)	入口MCB濃度100 ppm			入口MCB濃度18 ppm		
	実施例14	比較例13	比較例14	実施例14	比較例15	比較例16
触媒C	触媒H	触媒K	触媒C	触媒H	触媒K	
1	99.3 (99.3)	16.0 (16.0)	34.5 (34.5)	99.7 (16.0)	85.2 (13.6)	86.5 (13.8)
25	94.3 (94.3)	49.0 (49.0)	51.1 (51.1)	99.9 (16.0)	84.2 (13.5)	85.9 (13.7)
50	92.0 (92.0)	52.9 (52.9)	53.2 (53.2)	99.8 (16.0)	83.8 (13.5)	85.2 (13.6)
76	91.1 (91.1)	52.8 (52.8)	53.5 (53.5)	99.8 (16.0)	83.6 (13.4)	84.8 (13.6)
100	91.4 (91.4)	46.9 (46.9)	52.9 (52.9)	99.4 (15.9)	83.1 (13.3)	84.6 (13.5)
125	90.8 (90.8)	50.2 (50.2)	53.7 (53.7)	—	—	—
150	81.0 (81.0)	52.8 (52.8)	58.9 (58.9)	—	—	—
175	80.6 (80.6)	50.9 (50.9)	53.5 (53.5)	—	—	—

括弧内はMCB分解によるHCl生成量 (ppm) を示す。

【0054】5) SO₂酸化活性試験

触媒A、GまたはJを30mmΦの筒状ガラス製反応器に10m³の容積を占めるように詰め、二酸化硫黄O₂1容量%を含む、酸素10容量%、窒素79.9容量%、水蒸気10容量%の組成のガスを連続的に流し、空間速度5000h⁻¹、反応温度140～180°Cで5*

*時間反応させた。5時間反応経過時のデータを表5に示す。二酸化硫黄の酸化率(%)は、[(入口SO₂濃度-出口SO₂濃度)/(入口SO₂濃度)] × 100の計算式により求めた。

【0055】

【表5】

表5

	触媒	反応温度 (°C)	SO ₂ 酸化率 (%)
実施例16	A	180	0.4
実施例17	A	160	0.0
実施例18	A	140	0.0
比較例17	G	180	2.5
比較例18	G	160	1.6
比較例19	G	140	1.2
比較例20	J	180	3.3
比較例21	J	160	2.4
比較例22	J	140	1.8

【0056】6) プロムベンゼンの分解活性試験

触媒AまたはGを30mmΦの筒状ガラス製反応器に10m³の容積を占めるように詰め、プロムベンゼン(MB)16ppmを含む酸素10容量%、窒素90容量%の組成のガスを連続的に流し、空間速度6000h⁻¹、反応温度140～160°Cで5時間経過時のデータ※

※を表6に示す。MBBの分解率(%)は、[(入口MBB濃度-出口MBB濃度)/(入口MBB濃度)] × 100の計算式により求めた。

【0057】

【表6】

表6

	触媒	反応温度 (°C)	MBB分解率 (%)
実施例19	A	180	98.8
実施例20	A	160	98.5
実施例21	A	140	98.1
比較例23	G	180	85.5
比較例24	G	160	80.8
比較例25	G	140	77.2

【0058】

★て、より高い活性及び耐久性が得られる触媒を安価に提供することができる。更に、本発明によれば、この触媒シンなどの有機塩素化合物を含むガスの浄化処理において★50を用いた有機ハロゲン化合物の効率良い分解方法を提供

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することができる。

【0059】特に本発明にかかる触媒は、有機ハロゲン化化合物の分解において、活性、耐久性及び耐SO₂性に優れているだけでなく、SO₂のSO₃への酸化を実質的に生じさせず、しかもHC1に対しても耐久性がある

ので、ダストが共存する場合や、処理対象のガスがSO_x、HC1を含む、あるいは分解処理領域内にこれらが発生する場合における有機ハロゲン化化合物の効率良い分解に有効に利用できる。

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